EXHAUSTIVE FRACTIONATION OF THE "EXTRACT" PORTION OF THE LUBRICANT FRACTION FROM A MIDCONTINENT PETROLEUM [1]*

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ABSTRACT

This paper describes the separation, by distillation and extraction, of the extract portion of the lubricant fraction from a midcontinent petroleum. After a preliminary separation of the "asphaltic" material, the remainder of the sulfur dioxide-soluble material and the silica gel "hold-up" were combined and systematically distilled until substantially constant-boiling fractions were obtained. Five charges of these fractions with narrow-boiling ranges were then prepared and each charge of from 500 to 700 g was separated into 30 to 40 fractions by reflux extraction with methyl cyanide, or methyl cyanide containing acetone, in 16.7-m columns. Kinematic viscosities at 100° and 210° F, refractive indices, densities, refractive dispersions, specific optical rotations, and aniline points were determined for most of the fractions from the extraction process. In addition, for 41 "key" fractions there are reported boiling points, molecular weights, and carbon-hydrogen ratios, and for some of these fractions there are given the percentages of sulfur, nitrogen, and oxygen. Attention is called to a number of interesting facts in connection with the properties of these petroleum fractions.

CONTENTS

I. INTRODUCTION

Two years ago this laboratory reported the results of an investigation [1, 2][3] of the chemical composition of a "water-white" oil prepared from the lubricant fraction of a midcontinent petroleum. To obtain a more complete picture of the whole lubricant fraction of petroleum, a similar investigation has been made on portions of the same fraction which were soluble in sulfur dioxide and retained by silica gel. After a preliminary separation of the asphaltic material, the remainder of the sulfur dioxide extract and the material retained by silica gel were combined and then separated, first by repeated distillations in high vacuum and then by extraction with methyl cyanide.

A correlation of the physical properties of certain fractions from this extraction process, and their comparison with those obtained in the investigation of the water-white oil and with synthetic hydrocarbons, follow in a subsequent paper.

II. ORIGIN OF THE MATERIAL AND OUTLINE OF THE INVESTIGATION

The lubricating-oil stock came from well No. 6 of the South Ponca Field, Kay County, Okla. Before delivery to the Bureau, the oil was distilled in vacuo by the Sun Oil Co., Philadelphia, Pa. Treatment of the oil at this Bureau has been described elsewhere [1, 2, 3] and is illustrated diagrammatically in figure 1. It consisted in (1) The separation of an extract portion by extraction with liquid sulfur dioxide at room temperature, (2) the separation of a "wax" portion by crystallization from ethylene chloride at −18° C, and (3) the separation of the remainder into two portions by filtration through silica gel: (a) a water-white portion, whose investigation has already been reported [1, 2], and (b) a portion recovered from silica gel and listed in figure 1 as silica gel hold-up.

This paper deals only with the investigation of the sulfur dioxide-soluble portion and the silica gel hold-up. As shown in figure 1, the present fractionation was begun by separating the extract portion into two parts by extraction with sulfur dioxide and petroleum ether at −55° C. The portion soluble in sulfur dioxide at −55° C, denoted in figure 1 as asphaltic material, was placed in storage. The petroleum ether-soluble portion was combined with the material recovered from silica gel and the mixture submitted to a systematic fractional distillation in high vacuo. After the distillation had progressed as far as was profitable, fractions, represented in figure 1 as distillation keys, were selected and a number of their physical properties determined. Five charges, designated as *A, B, C, D,* and *E,* of from 500 to 700 g each, were then prepared for extraction by mixing according to their viscosities the individual distillation fractions of about 70 g each. These charges amounted to a little less than one-third of the total weight of the distillate and represented the greater part of the distillation range. Each charge was separated into 30 to 40 fractions of about 15 g each by extraction with methyl cyanide, or with methyl cyanide containing some acetone for the less soluble fractions. Kinematic viscosities at 100° and 210° F, and refractive indices at 25° C, were determined on all the fractions from the extractors. Densities,

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[3] Figures in brackets indicate the literature references at the end of this paper.
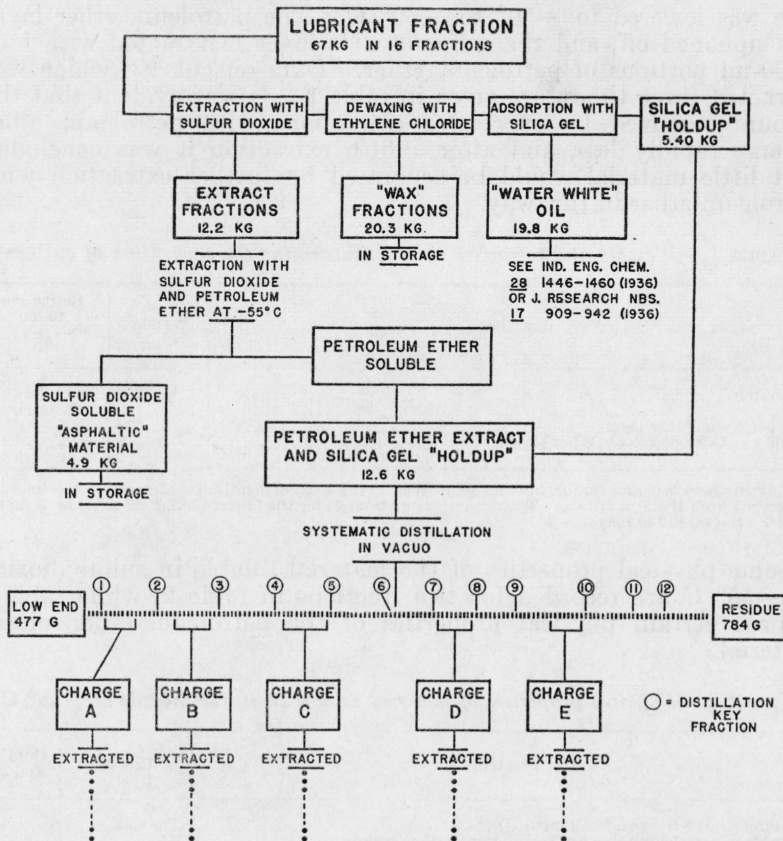
FIGURE 1.—*Chart showing treatment and disposition of lubricating-oil fractions.*

refractive dispersions, aniline points, and optical rotations were determined on most of them. In addition, carbon-hydrogen ratios, molecular weights, and boiling points were determined on 41 key fractions, and on some of these the percentages of sulfur and nitrogen were also determined.

III. PRELIMINARY TREATMENT BEFORE DISTILLATION

1. SULFUR DIOXIDE-SOLUBLE PORTION

It seemed probable that the extremely viscous, semisolid material contained in the sulfur dioxide-soluble portion would be difficult to "degas", would probably froth and bump in the stills, and make difficult, if not impossible, the operation of the extractors. To avoid these difficulties a preliminary separation was made:

In a 3-liter Pyrex flask about 500 to 600 g of oil was obtained in solution (or suspension) in 1,600 ml of petroleum ether (bp 30° to 60° C), by vigorous stirring at room temperature. The temperature was lowered to about −15° C, at which point 500 ml of liquid sulfur dioxide was added, and, while still stirring vigorously, the tempera-

ture was lowered to −50° to −60° C. The petroleum ether layer was siphoned off, and the sulfur dioxide layer reextracted with four 1,500-ml portions of petroleum ether. Data on cut 23, which was extracted three times, are given in table 1. It was evident that the amount removed by successive extractions with petroleum ether became rapidly less, and after a fifth extraction it was concluded that little material would be separated by further extraction with petroleum ether in this way.

TABLE 1.—*Weights and refractive indices illustrating the separation of cut 23*[a]

Fraction	Weight	Refractive index n_D^{28}
	g	
SO₂-soluble	279	Too dark to measure.
First petroleum ether layer	308	1.578.
Second and third petroleum ether layers	108	1.586.

[a] Cut numbers here and throughout this paper refer to the original identification marks on the fractions as received from the Sun Oil Co. These numbers go from 23 for the lowest-boiling material to 38 for the highest. See table 2 in reference [3].

Some physical properties of the material soluble in sulfur dioxide at −55° C are recorded for two fractions in table 2, while table 3 records certain physical properties of the petroleum ether-soluble material.

TABLE 2.—*Physical properties of material soluble in sulfur dioxide at −55° C*

Fraction	Cut 23	Cuts 37 and 38
Softening point [a] (ring-and-ball method) (° C)	Too soft	49. 6
Insoluble in petroleum ether [a] at room temperature (percent)	8.5	37. 8
Refractive index (n_D^{15}) of the portion soluble in petroleum ether	1.66	1. 67

[a] The data on softening point and insoluble in petroleum ether recorded in this table were obtained by O. G. Strieter, Research Associate at the National Bureau of Standards, representing the Asphalt Shingle and Roofing Institute.
[b] This petroleum ether distilled from 35° to 60° C.

TABLE 3.—*Physical properties of the portion soluble in petroleum ether*

Fraction	Kinematic viscosity at		Kinematic-viscosity index	Refractive index n_D^{15}
	100° F	210° F		
	Stokes	*Stokes*		
Cut 24	1. 37	0. 0736	−148	1. 573
Cut 30	4. 09	. 121	−192	1. 575
Cut 35+36	49. 1	. 445	−184	1. 568

2. MATERIAL RECOVERED FROM SILICA GEL

The silica gel hold-up was extremely dark in color, so, with a small portion, an attempt was made to remove black asphaltic material by treatment with sulfur dioxide and petroleum ether at −55° C. However, since practically the entire fraction was found to be soluble in the petroleum ether layer, this treatment was not continued.

Certain physical properties of the silica gel hold-up are given in table 4. It was not possible to get refractive indices with any high degree of precision, owing to the highly colored nature of this material.

TABLE 4.—*Physical properties of silica gel hold-up*

Fraction	Kinematic viscosity at—		Kinematic-viscosity index	Refractive index n_D^{25}
	100° F	210° F		
	Stokes	*Stokes*		
Cut 23 to 28	2.93	0.127	−52	1.54 to 1.55
Cut 29 to 32	6.81	.182	−95	1.54 to 1.55
Cut 33 to 38	8.85	.261	−3	1.52 to 1.53

3. COMBINATION OF THE MATERIAL SOLUBLE IN PETROLEUM ETHER WITH THAT RECOVERED FROM SILICA GEL

The silica gel hold-up and the petroleum ether-soluble portion of the extract were now combined into three charges for distillation and some physical properties of these charges determined. These properties are given in table 5.

TABLE 5.—*Properties of the petroleum ether-soluble portion combined with the portion retained by silica gel*

Fraction	Kinematic viscosity at—		Kinematic-viscosity index	Refractive index n_D^{25}	Sulfur content	Nitrogen content
	100° F	210° F				
					Percent by wt	*Percent by wt*
	Stokes	*Stokes*				
Cut 23 to 28	2.97	0.113	−123	1.562	0.94	0.14
Cut 29 to 32	7.23	.171	−153	1.568	.98	.10
Cut 33 to 38	18.84	.322	−82	1.557	.87	.14

IV. DISTILLATION EQUIPMENT AND PROCEDURE

The oil was systematically distilled in a battery of six simple molecular stills of the type used in the distillation of the water-white oil [3]. These stills were 12 cm in diameter and were charged with 420 to 500 g of oil. Each charge yielded six distillate fractions and one residue, each of 60 to 70 g. The receivers, one of which is shown schematically in figure 2, were of the type previously described, but modified to permit the removal of fractions with a siphon. Referring to figure 2, oil from the still flowed through tube B to funnel C, and then to one of the six (only two are shown) receivers, D. The funnel contained a soft-iron core and was directed to the individual receivers by the action of an Alnico magnet on this core. The fractions were transferred to the sample bottles by means of a siphon, inserted through the ground joint A and extending to the well in the bottom of each receiver. This procedure has two advantages: The oil does not at any time come into contact with the ground joints; leakage is minimized by the reduction in number, from six to one, of ground joints for each receiver.

There was a drainage problem with this very viscous oil, and consequently tube B through which the distillate passed to the receiver, was electrically heated nearly to the temperature of distillation. Also to cause the oil to drain as completely as possible, the receivers were surrounded with beakers of water kept at 90° C, and at least an hour was allowed between the time of removal of the bulk of the sample and the removal of the drainage. Auxiliary equipment was used to heat the siphons to avoid drainage losses. Precautions were also taken to avoid large losses in transferring the oil from the sample bottle to the stills. The sample bottles were heated in a special container on the steam bath so that the entire bottle up to the neck was hot, and as much oil as possible was transferred to the still. The oil still retained in the bottles, constituting a single charge, was washed out with ether, the ether removed, and the oil transferred to the still by means of a small flask.
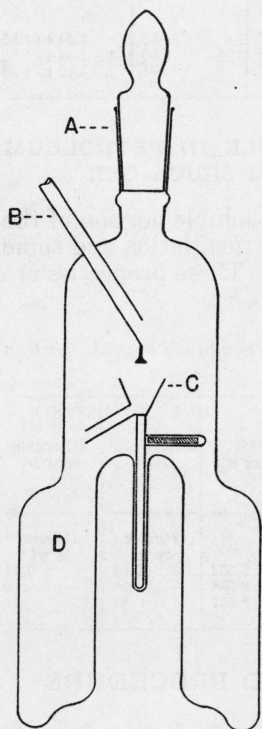
During the first distillation considerable difficulty was experienced with frothing and sputtering, which may have been due to small traces of petroleum ether which had not been completely removed. After this distillation little difficulty was experienced except with a few of the most viscous charges. The procedure adopted to avoid frothing was to reduce the viscosity of the oil by warming it to about 40° to 60° C below its distillation temperature, and then to reduce the pressure slowly.

A period of about 7 hours was required for charging the stills and degassing the charges, and an equal period for the distillation of the six fractions. The noncondensible gas pressure as read on a McLeod gage was usually about 10^{-4} mm Hg. The temperature of distillation varied from 95° C for the lowest-boiling fractions to about 210° C for the highest-boiling fractions. The highest temperature of distillation of any fraction subsequently extracted was about 170° C. After a distillation had been completed, carbon dioxide was admitted to the system, and the fractions were stored in an atmosphere of carbon dioxide until the next distillation. The color of the distillation fractions varied as the boiling point increased from yellow to deep orange red. The black material originally present remained in the residues from the distillation.

FIGURE 2. *Receiver for vacuum distillation.*

As with the water-white oil, the viscosity of the distillation fractions increased continuously with increase in boiling point, and consequently viscosity was used as the basis for mixing fractions for successive distillations. The viscosity at 210° F was used primarily for this purpose, since less material was retained by the pipettes at this higher temperature.

On the right of figure 3 are shown the ranges of viscosities of the fractions which were mixed to prepare some of the charges for the eighth distillation, while in the main part of the figure the viscosities of the fractions resulting from this distillation are plotted with respect to the percentage of the charge distilled. The range in viscosity of the fractions resulting from the distillation of any one charge was not much greater than the range in viscosity of the fractions mixed to prepare the charge, and it was therefore considered unprofitable to continue further the distillation.

Although the range in viscosity of the fractions from the more viscous charges is much greater than that for the fractions from the
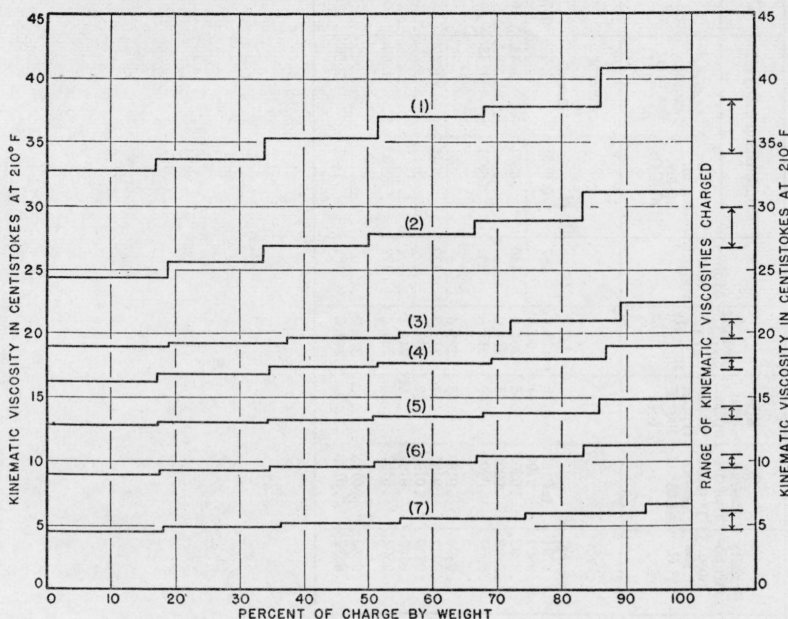
FIGURE 3. *Viscosities of fractions from the final distillation.*

less viscous charges, the ranges in boiling point of the two series of fractions do not differ greatly. Thus, the ranges in boiling point of the fractions given in curves (2) and (6) of figure 3 (computed from figure 4) are about the same, namely, 10° C.

After the eighth distillation, there were 144 fractions (see fig. 1) with a total weight of 9,970 g, an undistilled residue of 784 g, and a more volatile portion of 477 g, removed at earlier stages from the systematic distillation.

V. PROPERTIES OF DISTILLATION FRACTIONS

Before proceeding to the extraction process, certain properties were determined on 12 selected distillation fractions, covering practically the entire boiling range. These distillation key fractions are indicated in figure 1, and their properties are listed in table 6.

TABLE 6.—*Physical properties of distillation key fractions*

Key fraction (see fig. 1)	Kinematic viscosity at 100° F	Kinematic viscosity at 210° F	Kinematic-viscosity index	Refractive index n_D^{25}	Density at 100° F	Density at 210° F	Density extrapolated 77° F = 25° C	Refractive dispersion $n_F - n_C$ at 25° C	Specific optical rotation at 100° F $[\alpha]_D$	Boiling points at 1 mm Hg	Molecular weight	Ratio: moles H_2O/CO_2	Mass of sample less mass of C+H	S	N	O by diff.	n	x	Aniline points
	Stokes	*Stokes*			*g/ml*	*g/ml*	*g/ml*			*°C*			*Percent by wt of sample*						*°C*
1	0.687	0.0559	−88	1.5590	0.9705	0.9299	0.9794	0.0195	+0.19	176.6	287	0.6861	1.26	0.76	0.03	0.47	21.1	−13.3	7.2
2	1.76	.0849	−136	1.5634	.9780	.9362	.9869	.0199	.41	196.6	------								12.7
3	2.84	.105	−159	1.5648	.9803	.9392	.9892	.0202	.55	204.6	330	.6861	1.44	.93	.04	.47	24.3	−15.2	16.8
4	4.09	.126	−161	1.5630	.9794	.9374	.9883	.0200	.63	214.0									20.3
5	5.68	.145	−181	1.5650	.9815	.9398	.9904	.0200	.69	218.8	351	.6931	1.42	.94	.07	.41	25.8	−15.8	21.5
6	6.80	.167	−148	1.5629	.9810	.9367	.9899	.0199	.58	225.6									23.5
7	(8.90)	.189	−158	1.5629	.9823	.9381	.9912	.0197	.57	232.2	372	.7045	1.49	.88	.09	.52	27.3	−16.1	28.3
8	10.8	.213	−147	1.5622	.9770	.9371	.9859	.0199	.62	238.1									30.3
9	14.3	.244	−154	1.5625	.9799	.9374	.9888	.0197		244.1									32.6
10	28.9	.353	−153	1.5630	.9803	.9364	.9892	.0197		260.6	429	.7132	1.62	.94	.14	.54	31.4	−18.0	37.8
11	38.9	.442	−116	1.5592	.9774	.9338	.9863	.0193		275.7									45.9
12	50.0	.540	−85	1.5570	.9728	.9308	.9817	.0189		289.2	491	.7387	1.56	.83	.18	.55	35.9	−18.7	52.6

The methods and apparatus for determining these properties are discussed in section VIII, p. 548.

It may be noted that the molecular weight, viscosities, and aniline points increase with increasing boiling point. The refractive indices, densities, and refractive dispersions of the first and last fractions are somewhat lower than those of the rest, while the viscosity indices are higher. This variation is, however, negligible when compared with the large variations produced by the subsequent extraction process, and indicates that substantially no type separation was effected by distillation. The optical rotation increases up to about the third key
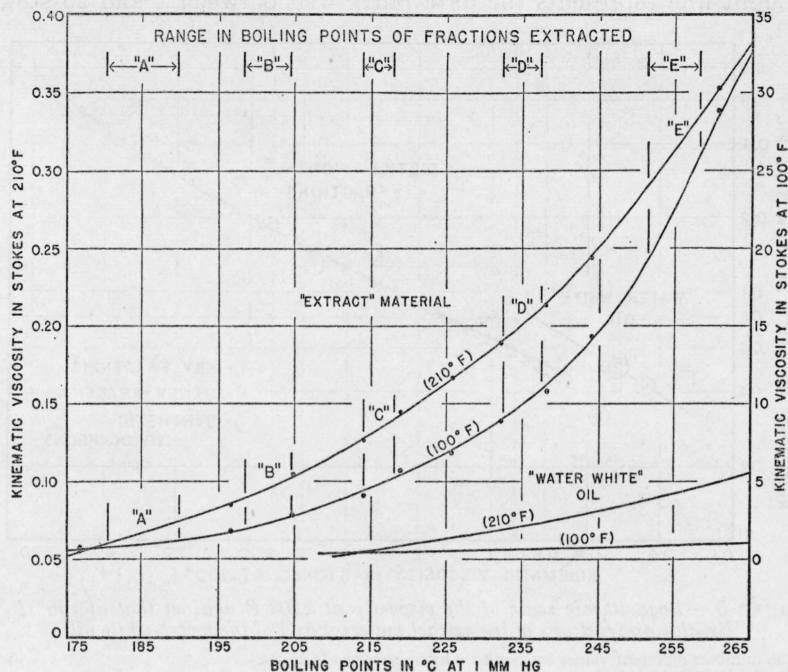
FIGURE 4.—*Relations between viscosity and boiling point for distillation fractions of the extract material and of the water-white oil.*

The boiling-point ranges of the fractions mixed to prepare the changes for extraction are also shown.

fraction and from there on remains substantially constant to the eighth key fraction.

It is to be noted that these fractions contain from 1.2 to 1.6 percent by weight of elements other than hydrogen and carbon. The sulfur and oxygen contents do not vary greatly throughout these fractions, but the nitrogen content increases from 0.03 to 0.18 percent with increase in molecular weight. Although the percentage of hydrogen increases from 10.1 to 10.8 from the first to the twelfth fraction, the deficiency of hydrogen as given by the x value in the formula C_nH_{2n+x} increases from -13.3 for the first to -18.7 for the twelfth fraction.

Some of the relationships between physical properties are shown graphically in figures 4 and 5. In figure 4 are also shown the relationships between boiling point and viscosities at 100° and at 210° F for distillation fractions of the water-white oil [3]. It has been observed

by other investigators that the viscosities of extract fractions for given boiling points are much higher than those of raffinate fractions, and a comparison of the viscosities of these extract fractions and water-white oil fractions once more emphasizes this point. There is also shown in figure 4 the range in boiling points and viscosities of the fractions subsequently mixed to prepare for the extractors charges *A*, *B*, *C*, *D*, and *E*.

In figure 5 are plotted on a logarithmic scale the viscosities at 210° F with respect to those at 100° F for a number of the distillation fractions. The points fall on a line with only a slight curvature. Indeed, a straight line represents the data fairly well between 2 and 25 stokes
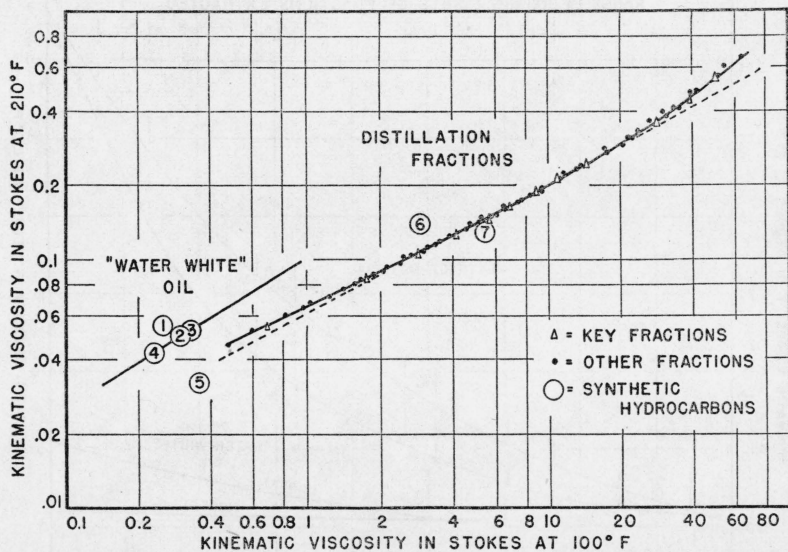
FIGURE 5.—*Logarithmic scale of the viscosity at 210° F against that at 100° F for distillation fractions of the extract material and of the water-white oil.*

The numbers represent values for synthetic hydrocarbons as follows:
(1) 16-*n*-Butylhentriacontane.
(2) 1-Cyclohexyl-2-hexahydrobenzylheptadecane.
(3) 1,1-Dicyclohexylhexadecane.
(4) 1,1-Diphenylhexadecane.
(5) Dihydrodiethylanthracene.
(6) Dihydrodi-B-octylanthracene.
(7) Dihydrodiisoamylanthracene.

at 100° F. Below and above these viscosities the deviation from the linear becomes more pronounced. These deviations correspond with the lower refractive indices, lower dispersions, and higher viscosity indices found for these fractions, and indicate a slight change in the type of material. Also shown in this figure for comparison is a plot of the viscosities of the water-white oil distillation fractions and several synthetic hydrocarbons.[4] A plot of this nature is useful in checking errors in the determination of viscosity. In cases where large deviations from these curves were found redetermination invariably brought the points closer to the curve.

[4] The values for the synthetic hydrocarbons were obtained by interpolation or extrapolation with the aid of Cragoe's equation [4] from the original data, which extended from approximately 20° to nearly 100° C, of Suida and Planckh [5] for 16-*n*-butylhentriacontane; Landa and Cech [6] for 1,1-dicyclohexylhexadecane, 1-cyclohexyl-2-hexahydrobenzylheptodecane, 1,1-diphenylhexadecane; and Lerer [7] for dihydrodiethylanthracene, dihydrodi-*β*-octylanthracene, and dihydrodiisoamylanthracene.

VI. PRELIMINARY EXPERIMENTS WITH SOLVENTS

Acetone, the solvent used in the extraction of the water-white oil, could not be used with the oil under investigation, because of the high solubility of the oil in it. Consequently, a few preliminary experiments were made to determine the solubility of the material under investigation in a number of solvents and to obtain an approximate measure of the selectivity of the solvents. These experiments were confined to low-boiling solvents which could be readily removed from the oil.

Two fractions were used in this work: One, having a kinematic viscosity of 0.0244 stoke at 210° F, came from the low-boiling end of the distillation range and had a boiling point below 175° C at 1 mm Hg; the other, having a viscosity of 0.275 stoke at 210° F, came from well up in the distillation range and had a boiling point of 249° C at 1 mm Hg.

The results of the solubility and selectivity tests shown in table 7 were obtained by shaking the oil and solvent in a separatory funnel, separating the phases, and removing the solvent. After reading the refractive indices, the dissolved and undissolved portions were recombined and the same oil was used with the next solvent.

TABLE 7.—*Results of preliminary experiments with several solvents*

Fraction	Weight	Refractive index n_D^{25}	Solvent	Volume of solvent	Temperature
Original oil (KV_{210}=0.0244)	g 75	1.5368		ml	$°C$
Undissolved	12	1.5098	}Methyl formate	450	+15
Dissolved	63	1.5436			
Undissolved	43	1.5199	}Methyl cyanide	450	+30
Dissolved	31	1.5637			
Undissolved	30	1.5247	}Acetone+Water [a]	155	0
Dissolved	43	1.5474			
Undissolved	44	1.5284	}Methyl alcohol	450	+25
Dissolved	24	1.5518			
Undissolved	34	1.5120	}Sulfur dioxide	150	−25
Dissolved	34	1.5620			
Original oil KV_{210}=0.2753	54	1.5630			
Undissolved	47	1.5579	}Methyl cyanide	450	+30
Dissolved	7	1.6117			
Undissolved	29	1.5498	Acetone,[b] +	200	} +25
Dissolved	25	1.5789	Water	5	

[a] Completely miscible in pure acetone to −25° C. This 155 ml of solvent was composed of 150 ml of acetone plus 5 ml of water.
[b] Completely miscible in pure acetone at room temperature.

It is evident from the data in table 7 that the lower-boiling fraction is too soluble in either sulfur dioxide or acetone to permit the use of these solvents at room temperature. The use of solvents at much below room temperature in the type of columns used (see p. 546) is considered impractical, owing to the extremely high viscosity of this oil at low temperatures. Methyl formate also dissolves too much of the lower-boiling fraction, and is excluded, moreover, because its density (D_{20}=0.975) is between that of the fractions (D_{25}=0.85—1.08) obtained in the systematic extraction. From the point of view of solubility (at least for the lower-boiling fractions), both methyl alcohol and methyl cyanide appear satisfactory.

To determine the relative selectivity of solvents, some physical property which changes markedly with type of molecule should be compared for equal percentages extracted. While such data have not been obtained, it is possible to get some idea as to the selectivity from the spread in refractive indices given in table 7. It is evident that methyl cyanide is more selective than methyl alcohol, and at least as selective as any of the other solvents tested, with the exception of sulfur dioxide.

Preliminary experiments indicated that a short extractor operated satisfactorily with the lower-boiling fractions when used with pure methyl cyanide. However, with the higher-boiling fractions, a mixture containing 20 to 30 percent of acetone was required to obtain satisfactory operation.

VII. EXTRACTION EQUIPMENT AND PROCEDURE

The extractor columns used in this investigation were essentially the same as those used in the extraction of the water-white oil with acetone [1]. This type of column has been described by Cannon and Fenske [8]. The columns were increased in height to 16.7 m. When filled with water, most of the flasks at the bottom of the extractors broke. The old flasks were replaced with heavy-walled Erlenmeyer flasks (500 ml) set in plaster of paris and mounted on an iron frame. Additional capacity was obtained by sealing tubes 4 cm in diameter and 10 cm long to the neck of the Erlenmeyer flask rather than by using Erlenmeyer flasks with larger bases. Also, the bottoms of the Erlenmeyer flasks were blown slightly convex. With these changes the vessels withstood the hydrostatic pressure, and no breakage occurred throughout the work.

It had also been found in preliminary work with a short extractor column that considerable color was produced in the fractions. This production of color was undoubtedly due to oxidation, since it was very materially reduced by maintaining an atmosphere of carbon dioxide over the boiling methyl cyanide. Throughout the systematic extraction a stream of carbon dioxide, under a head of 10 mm of oil, was passed through the top of the condenser.

The operation of the extractor columns was essentially the same as with the water-white oil and acetone. The extraction of charges A, B, and C was begun with pure methyl cyanide (constant-boiling from a 30-plate column). For charges D and E, because of the somewhat lower solubility of this material, a mixture of 75 percent of methyl cyanide plus 25 percent of acetone was used at the beginning. In the extraction of charges A, B, and C the reflux of oil globules was quite as satisfactory as was obtained with the water-white oil and acetone. However, for a number of the fractions at the beginning of the extraction of D and E, only a small part of the reflux returned as globules, since the greater part formed a stream which flowed down the walls of the column. This condition is undoubtedly associated with the extremely high viscosity of the first few fractions from these extractors (E–9 has a viscosity of 886 stokes at 100° F.) It was not until about the fifth fraction for extractor D, and the twelfth fraction for extractor E, that these columns began to function normally.

Throughout the greater part of the extraction of a charge, it is possible to control the size of the fractions simply by varying the amount

of methyl cyanide in the boiler (100 to 400 ml). There is, however, a certain point where the solubility becomes so low that even with the boiler full (400 ml) the size of the oil fractions is too small, and it becomes advisable to change or modify the solvent. It should also be pointed out that when the solubility becomes too low (that is, below about 0.8 to 1 g per 100 ml of methyl cyanide) the column does not operate satisfactorily. Consequently, after removal of fraction "*A–29*", 300 ml of acetone instead of methyl cyanide was charged into the column and the extraction completed by adding acetone instead of methyl cyanide. For extractor *B*, 350 ml of acetone was charged at fraction 32, and from this fraction to the end of that series an attempt was made to regulate the size of the oil fractions by charging, as seemed desirable from the weight of the preceding fraction, either methyl cyanide or acetone or a mixture. The same procedure was adopted for extractor C at fraction 29.

For extractors *D* and *E*, as mentioned previously, a mixture of 75 percent of methyl cyanide with 25 percent of acetone by volume was used at the beginning. At *D–24* and *E–20*, the size of the fractions was controlled by increasing the percentage of acetone. Even with this procedure, the decrease in solubility for the last few fractions from all of the extractors was usually so pronounced that it was necessary in some cases to combine adjacent fractions to obtain a portion as large as was required. In operating a column of this type with a mixture, it can be seen that when equilibrium is reached the concentration of acetone in methyl cyanide will be constant throughout the column except for the boiler, where a higher percentage of the higher-boiling component (methyl cyanide) will exist. Hence, since the oil-solvent fractions removed from the boiler were richer in methyl cyanide, the concentration of acetone in columns *D* and *E* undoubtedly increased above the average of 25 percent by volume.

After reflux commences, the less soluble portion returns to the oil reservoir and the more soluble oil takes its place; consequently, there is an increase in the density of solution in the reflux leg of the extractor. To balance this increase in density, an increase in the hydrostatic head in the solvent leg is necessary. When equilibrium is reached there should be no further increase in density in the reflux leg, and the liquid level in the solvent leg should reach (if no other factors were to be considered) a constant maximum. For extractor *A* this maximum occurred about 16 hours after reflux commenced, and the height was fairly constant. Other factors, however, influence this height, such as rate of circulation of solvent and viscosity of the oil in the reservoir, and, since a few degrees drop in temperature cause a pronounced increase in viscosity, this height was not very constant for the other extractors, and the time, though longer than for extractor *A*, could not be accurately determined. To be on the safe side, 24 hours was allowed for equilibrium for extractors *A* and *B*, 36 hours for *C* up to fraction 7 and from this point on, 24 hours, 48 hours for *D* and *E* up to fractions 5 and 7, respectively, when they were put on a 36-hour schedule to fractions 18 and 17 and from there on, 24 hours.

The solvent was removed from the fractions by maintaining them at 100° to 110° C in a stream of carbon dioxide for 2 to 3 hours. The pressure was then reduced to 27 mm, and sweeping out with carbon dioxide at the same temperature was continued for an additional 2 to 3 hours.

The fractions were stored in an atmosphere of carbon dioxide in small glass bottles fitted with rubber stoppers which had been boiled with a solution of sodium hydroxide to remove free sulfur. After about 2 months there were again signs of sulfur appearing on some of the stoppers, so they were replaced with Neoprene stoppers. There was no evidence of contamination of the samples by the stoppers.

VIII. DETERMINATION OF PROPERTIES

In general, the same methods of determining the physical constants were used as with the water-white oil [1, 2]. However, complications were introduced in many cases by the extreme viscosity of some of the fractions, their high temperature coefficients of viscosity, their color, and by the fact that they contained sulfur and nitrogen.

1. VISCOSITY [5]

Kinematic viscosities were determined at 100° and 210° F with the aid of the assembly of viscosity pipettes previously described. The pipettes were furnished with removable sintered-glass filter tips and were filled by drawing the oil through these tips. Duplicate determinations were made, and the precision of the recorded results is considered to be about ±1 percent for the fractions with high temperature coefficients of viscosity and about ±0.2 percent for fractions with small coefficients. The temperatures of the baths were usually constant to within ±0.03° F. The equipment available was not satisfactory for determining the viscosity at 100° F of a few of the most viscous fractions from charges C, D, and E; consequently, their viscosities were not determined. Kinematic-viscosity indices were computed with the aid of the tables given by Hersh, Fisher, and Fenske [9].

2. DENSITY [6]

Densities of the distillation key fractions were determined at 100° and 210° F with the aid of the same series of viscosity pipettes, each value recorded being the result of two determinations agreeing within ±0.0003 g/ml. For the extraction fractions, owing to the very viscous nature of some of them, it was preferable to use a picnometer of about 8-ml capacity of the type shown in figure 6. After being filled, the picnometer was immersed to 8 mm from the calibration mark, and the upper end of the capillary tube, A, was warmed gently with a flame to reduce the viscosity and hasten drainage. With an eye dropper inserted in tube A, the oil level was adjusted to the calibration mark. Duplicate determinations were made, and a precision of ±0.0003 g/ml was obtained.

FIGURE 6.—*Picnometer for viscous oils.*

Densities of five samples, C-1, D-1, E-1, E-8, and E-13, which were thought to be too viscous to observe in the picnometer, were determined by weighing in water by the Bureau's Capacity and Density Section. The results for these fractions are believed to be accurate to ±0.002 g/ml.

3. REFRACTIVE INDEX AND REFRACTIVE DISPERSION

Refractive indices were obtained with an Abbe refractometer. Refractive dispersions were obtained from readings on the compensator drum of the same instrument and the accompanying tables. Because of the color of the material, the precision of the refractive indices varies from about ±0.0003 for the first fractions from the extractors to about ±0.0001 for the last fractions. In a few cases, where intensity of color caused a lower precision, the values are bracketed. The refractive dispersions are believed to cover about the same range of precision, that is, from ±0.0003 to ±0.0001. In the work with the water-white oil [2], values for the Lorentz-Lorenz specific dispersion $(n_F^2-1)/(n_F^2+2)$ $-(n_C^2-1)/(n_C^2+2)\times1/d$ were computed from the values for n_F-n_C given by the Abbe refractometer. This was done to be consistent, since the Lorentz-Lorenz expression $(n_D^2-1)/(n_D^2+2)\times1/d$ (desired because of its use in determining the number of naphthene rings per molecule, as described by Vlugter, Waterman, and Van Westen [10]) had been used for the specific refraction. However, since the computation of the Lorentz-Lorenz specific dispersions from n_F-n_C is a tedious process, and since many of the data in the literature are given in terms of the simpler expression of Gladstone and Dale it has been used in this paper.

4. MOLECULAR WEIGHT

Molecular weights were determined by the ebullioscopic method [11], using benzene as the solvent. The results are considered accurate to within ±1 percent. Many of the samples were too viscous to introduce into the molecular-weight apparatus from a weighing pipette and were not sufficiently solid to add in the form of pellets. Small glass tubes having one end sealed and blown paper-thin were used for the introduction of these samples. Each tube was of such a diameter that it fell easily down the condenser but stuck at a constriction near the bottom of the condenser. The bottom end of the tube was then broken with a strong wire, and, after all the oil had been dissolved by the reflux and washed into the boiler, the remainder of the tube was caught in a hook and withdrawn. The molecular-weight equipment was checked during the course of this work with triphenylmethane. The value obtained for its molecular weight was 242.4, which is to be compared with the theoretical value of 244.3.

5. OPTICAL ROTATION

Both the viscosity and the color of the extraction fractions caused difficulties in the determination of optical rotation. At first, attempts were made to determine the activity of the undiluted oil in a 2-dm tube, as had been done with the water-white oil. However, striations, presumably due to the high viscosity, persisted in the oil and satisfactory fields were not obtained. By dissolving a weighed quantity of 7 to 10 g of the oil in 25 ml of benzene, and by using solutions of this concentration in a 4-dm tube, satisfactory fields were obtained and this procedure was therefore adopted. The high color of the fractions made reading of some fractions difficult with a 4-dm tube, and at the beginning a number of fractions *B–6, 13, 15, 21, 27, 31, 34, 37–38*, and residue *A–6, 17*, and residue were distilled in a small molecular still to

remove some of the color. In this distillation the fractions were taken practically to dryness, the greater part of the color being left in the few drops remaining in the still. Since practically the entire sample was distilled over, it is believed that this treatment did not appreciably alter the values for the optical rotation. Later it was found that satisfactory readings could be obtained on most of the samples with the aid of a stronger light source (500 watts). The other rotations were determined on undistilled samples, using a 500-watt bulb when necessary, with the exception of samples C-4 and E-8, which it was felt advisable to distil on account of their very dark color. Determinations of the optical rotation of the distillation key fractions were made on the undiluted oil at 100° F before the technique used for the extraction fractions had been developed. With this method it was not possible to determine optical rotation beyond distillation key fraction 8, either because of the high viscosity or the high color.

To determine whether the optical rotation was the same in benzene solution as in the undiluted oil, readings were made on one of the less viscous samples (A-residue) both in the undiluted form and in the form of solution. The values computed for $[\alpha]_D^{20}$ from the undiluted oil and from the solution were $+0.42$ and $+0.44$, respectively. The optical rotations were measured on a saccharimeter in the Polarimetry Section of this Bureau and converted from °S to $[\alpha]_D^{20}$. The values of $[\alpha]_D^{20}$ are believed to be precise to about ± 0.03.[7]

6. BOILING POINT [8]

Boiling points at 1-mm Hg pressure were determined, using a thermocouple calibrated by the Heat Division of this Bureau, in an apparatus which has been described previously [12].

7. ANILINE POINT

Aniline points were determined where possible with 1-ml portions each of oil and freshly distilled dry aniline. The sample was stirred and a slow stream of dry air passed over it. A precision of $\pm 0.1°$ C was obtained.

8. SOLUBILITY IN METHYL CYANIDE

Solubilities in methyl cyanide were determined by shaking a slight excess of the oil at about 40° C with methyl cyanide in a 50-ml glass-stoppered Erlenmeyer flask. The flask was then placed in a bath maintained at 25° C and left until the oil which precipitated had settled on the walls and bottom. 25 ml of clear solution was then transferred with a pipette to a 100-ml flask. The bulk of the solvent was removed by distillation and the last traces were pumped off. The gain in weight of the flask gave the weight of oil in 25 ml of solution. The results are believed to be accurate to within ± 0.03 g per 100 ml of solution.

9. CHEMICAL ANALYSIS

(a) CARBON AND HYDROGEN CONTENT

Combustion analyses were performed with the equipment used for the water-white oil [1], modified on account of the presence of sulfur

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[7] The authors are indebted to C. F. Snyder and W. W. Pigman for advice and assistance in this work. The authors are indebted to A. J. Streiff for assistance in this work.

and nitrogen. To remove the oxides of sulfur some of the copper oxide in the exit end of the quartz combustion tube was replaced with lead chromate on copper oxide, as described by Pregl [13]. This section of the furnace was maintained at about 500° C. For samples containing more than 0.05 percent of nitrogen, lead peroxide on asbestos, prepared as described by Pregl [14], was used. This preparation was contained in a separate tube attached to the main quartz combustion tube with a ground joint sealed with Cementyte. The body of the tube containing the lead peroxide was surrounded by a jacket in which p-cymene was refluxed, which gave a constant temperature near 176° C. Blank determinations were performed at frequent intervals and corrections usually amounting to about 0.0003 g for the Dehydrite tube and 0.0002 g for the Ascarite tube were necessary. Duplicate determinations were made with 0.5-g samples. The arithmetical average of the differences between duplicate determinations of the ratio moles H_2O/CO_2 was ± 6 parts in 10,000, exclusive of fraction A-27, for which the difference was ± 39 parts in 10,000. An uncertainty of 6 parts in 10,000 in the mass of water, or of carbon dioxide, corresponds to an uncertainty of about 0.006 percent by weight of hydrogen in the sample or about 0.05 percent by weight of carbon.

As a check on the accuracy of the combustion analyses, experiments were performed with known mixtures of cystine ($C_6H_{12}O_4S_2N_2$) and n-nonacosane ($C_{29}H_{60}$), the data for which are given in table 8.

Although the agreement between the values calculated and those found for the ratio moles H_2O/CO_2 is not very satisfactory, some of this difference may be due to impurities in the cystine. The agreement between the mass of the sample minus the mass of carbon plus hydrogen calculated and that found is reasonably satisfactory, and shows that the percentage of elements other than carbon and hydrogen in the oil samples may be calculated with an accuracy of about 0.04 percent by weight.

TABLE 8.—*Results which illustrate the accuracy of the combustion analyses*

Experiment	Nonaco-sane	Cystine	Ratio: Moles H_2O/CO_2		Mass of sample, less mass of $C+H$	
			Calculated	Found	Calculated	Found
	g	g			Percent by weight	Percent by weight
1	0.5014	0.0517	1.0333	1.0378	6.07	6.11
2	.5020	.0517	1.0333	1.0372	6.07	6.10

(b) SULFUR, NITROGEN, AND OXYGEN CONTENT [9]

The sulfur analyses were made by a method described by C. E. Waters [15]. The nitrogen was determined by the Kjeldahl method, using mercuric acetate as a catalyst with the addition of potassium sulfate. After digestion, the ammonia was distilled in a current of steam into $N/100$ HCl. The excess acid was titrated with $N/100$ NaOH, using methyl red as an indicator, with the solution at its boiling point.

[9] The authors are indebted to C. E. Waters for the sulfur determinations and to C. J. Rodden for the determinations of nitrogen.

The percentage of oxygen was obtained by subtracting the sum of the percentages of carbon, hydrogen, sulfur, and nitrogen from 100.

IX. TABULATION OF RESULTS

In table 9 are tabulated the kinematic viscosities at 100° and 210° F, the refractive indices, densities, refractive dispersions, specific rotations, and aniline points of many of the fractions from extractors *A*, *B*, *C*, *D*, and *E*. Data on the solubility of a few of the fractions in methyl cyanide are also given. Three derived quantities, kinematic-viscosity index, specific refraction, and specific dispersion, are also included in this table.

TABLE 9.—*Properties of fractions from final extraction process*

Fraction [a]	Percentage extracted [b]	Kinematic viscosity [c] at 100° F	Kinematic viscosity [c] at 210° F	Kinematic viscosity index	Refractive index [d] n_D^{25}	Density at 25° C [e]	Refractive dispersion n_F-n_C at 25° C	Specific optical rotation $[\alpha]_D^{29}$	Aniline point	Solubility in methyl cyanide at 25° C	Specific refraction [f] $\frac{n^2-1}{n^2+2}\times\frac{1}{d}$	Specific dispersion [f] $\frac{n_F-n_C}{d}$
		Stokes 0.75 to 1.30	*Stokes* 0.060 to 0.075			*g/ml*			°C	*g/ml of solution*		
Original charge [g]		(5.00)		(−108)	(1.561)	(0.983)	(0.0197)	(+0.27)	(9)		(0.329)	(0.0200)
[1]	8.6	5.00	0.0940	−634	1.6305	1.063				8.98	.3350	
2	11.6	3.87	.0856	−584	1.6317							
3	17.4	4.12	.0884	−578	1.6302							
4	23.4	3.99	.0882	−557	1.6202							
[5]	28.3	3.97	.0903	−514	1.6095	1.043	.0262				.3322	.0251
6	31.5	3.96	.0943	−447	1.5995					3.66	.3307	.0230
7	34.6	3.85	.0930	−447	1.5949	1.027	.0236					
8	37.4	3.71	.0950	−394	1.5897							
9	40.5	3.75	.0967	−378	1.5840							
[10]	43.3	3.43	.0946	−352	1.5798	1.010	.0212	+.13			.3294	.0210
11	46.0	3.13	.0939	−307	1.5746							
12	48.8	2.85	.0954	−243	1.5706				−5.2			
13	51.8	2.39	.0896	−219	1.5633							
14	54.4	2.16	.0872	−198	1.5578	.9861	.0174		+5.1		.3268	.0176
15	57.0	2.03	.0870	−173	1.5532							
16	59.5	1.65	.0824	−133	1.5465							
[17]	62.2	1.29	.0763	−97	1.5389	.9660	.0144	+.49	+18.0		.3242	.0149
18	64.7	1.16	.0743	−77	1.5344							
19	67.2	1.01	.0711	−59	1.5290							
20	69.6	.877	.0678	−42	1.5256	.9496	.0127		25.8	1.75	.3230	.0134
21	72.3	.714	.0640	−12	1.5215							
[22]	75.1	.620	.0602	−3	1.5188	.9363	.0121		31.3		.3241	.0129
23	77.4	.581	.0581	−3	1.5165							
24	79.9	.500	.0554	+17	1.5135							
25	82.3	.452	.0531	+25	1.5110	.9219	.0118	+.36	37.0		.3250	.0128
26	85.2	.400	.0508	+38	1.5076							
[27]	87.6	.362	.0496	+55	1.5058	.9097	.0115		39.7		.3265	.0126
28	90.0	.334	.0476	+58	1.5020	.9035	.0111	+.16	46.6	.95	.3266	.0123
29+30	92.7	.327	.0483	+71	1.4961	.8959	.0103		60.6		.3261	.0115
31+32	94.7	.305	.0471	+78	1.4837	.8818	.0087		84.8		.3243	.0099
33	95.8				1.4745			+.76	97.5			
[Res.]	100	.188	.0395	+137	1.4654	.8448	.0083	+.44	104.9	.09	.3275	.0098

Series A. Charge =581 g. Boiling-point range at 1 mm Hg=180.4° to 189.4° C

See footnotes at end of table.

TABLE 9.—*Properties of fractions from final extraction process*—Continued

Fraction [a]	Percentage extracted [b]	Kinematic viscosity [c] at		Kinematic viscosity index	Refractive index [d] n_D^{25}	Density at 25° C [e]	Refractive dispersion $n_F - n_C$ at 25° C	Specific optical rotation $[\alpha]_D^{20}$	Aniline point	Solubility in methyl cyanide at 25° C	Specific refraction [f] $\frac{n^2-1}{n^2+2}\times\frac{1}{d}$	Specific dispersion [f] $\frac{n_F-n_C}{d}$
		100° F	210° F									
		Stokes	*Stokes*			*g/ml*			°C	*g/ml of solution*		
		1.9 to 2.8	0.090 to 0.104	(−151)	(1.564)	(0.989)	(0.0201)	(+0.49)	(15)		(0.329)	(0.0203)
Original charge [e]												
1	2.4	36.2	0.170	−1590	1.6387							
[2]	7.6	26.7	.153	−1420	1.6397	1.071					.3362	
3	11.0	21.6	.148	−1210	1.6397							
4	14.8	19.6	.145	−1130	1.6368							
5	18.1	18.9	.144	−1100	1.6332							
[6]	21.4	18.7	.146	−1050	1.6306	1.061	.0300	−.02			.3355	.0283
7	23.7	(16.1)			1.6256							
8	25.8	16.9			1.6212	1.055	.0269				.3335	.0255
9	28.1	16.0	.150	−813	1.6155							
10	30.5	14.6	.157	−642	1.6098	1.045					.3316	
11	33.7	13.0	.150	−623	1.6016	1.037	.0246				.3307	.0237
12	36.4	12.0	.150	−560	1.5952	1.030	.0236				.3299	.0229
[13]	39.5	11.9	.151	−543	1.5903	1.026	.0222	+.30			.3292	.0216
[14]	42.1	10.5	.149	−473	1.5834	1.019	.0218				.3282	.0214
15	44.5	9.71	.149	−422	1.5820	1.016	.0211	+.36			.3286	.0208
16	47.2	8.31	.144	−369	1.5785	1.010	.0207		−3.5		.3287	.0205
17	49.8	6.95	.138	−318	1.5732	1.004	.0200				.3285	.0199
[19]	52.4	6.58	.134	−320	1.5695	0.9990	.0193	+.52	4.1		.3282	.0193
19	54.8	5.60	.130	−269	1.5652	.9942	.0187				.3277	.0188
20	57.4	4.74	.126	−221	1.5601	.9884	.0179				.3272	.0181
[21]	60.1	4.19	.123	−189	1.5558	.9837	.0173	+.80	13.0		.3267	.0176
22	62.9	3.19	.113	−148	1.5496	.9762	.0166				.3261	.0170
23	65.1	2.92	.111	−129	1.5466		.0159		20.2			
24	67.2	2.54	.106	−111	1.5416	.9673	.0150	+1.09	23.7		.3252	.0155
25	69.4	2.20	.103	−82	1.5349	.9613	.0139		27.0		.3238	.0145
26	71.0	1.73			1.5305	.9541	.0136		31.5		.3240	.0143
27	73.1	1.53	.0897	−51	1.5276	.9485	.0131	+1.10	34.1		.3244	.0138
[28]	74.8	1.24	.0843	−24	1.5229	.9439	.0125	+.97	36.5		.3236	.0132
29	77.1	1.08	.0793	−17	1.5196	.9388	.0123		39.2		.3236	.0131
30	79.0	0.925	.0744	−7	1.5168	.9336	.0120				.3240	.0129

Series *B*. Charge=605 g. Boiling-point range at 1 mm Hg=1.98.4° to 204° C

[31]	81.2	.786	.0711	15	1.5141	.9278	.0118	+.68	44.2		.3245	.0127
32	83.3	.689	.0673	24	1.5110	.9232	.0115				.3245	.0125
33	85.4	.599	.0637	35	1.5089	.9177	.0117		47.0		.3253	.0127
34	88.0	.516	.0602	48	1.5060		.0115	+.41				
[35]	90.1	.456	.0575	59	1.5027	.9051	.0112		51.3		.3265	.0124
36	92.2	.437	.0572	68	1.4999	.9005	.0110	+.27	55.3		.3266	.0122
37+38	94.5	.563	.0647	57	1.4930	.8976	.0092	+1.94	79.2		.3238	.0103
[Res.]	100	.309	.0506	104	1.4723	.8594	.0087	+1.31	106.0		.3260	.0101

Series *C*.   Charge=666 g.   Boiling-point range 1 mm Hg=214° to 218° C

Original charge		4.4 to 5.2	0.128 to 0.141	(−171)	(1.564)	(0.989)	(0.0200)	+(0.65)	(21)		(0.329)	(0.0202)
[1]	5.2		.340		(1.641)	1.076					.3353	
2	9.0	248	.311		1.6407							
3	12.3	158	.284	−2520	1.6366							
4	15.3	106	.275	−1750	1.6314			+.19				
[5]	17.9	97.8	.264	−1750	1.6278	1.061	.0298				.3343	.0281
6	20.6	84.1	.258	−1560	1.6248							
7	23.9	70.3	.253	−1340	1.6189							
[8]	26.9	56.2	.246	−1100	1.6126							
9	29.6	47.8	.241	−958	1.6081	1.041	.0264				.3321	.0254
10	32.0	42.3	.241	−827	1.6048		.0259					
11	34.6	36.8	.234	−750	1.5993	1.034	.0244	+.41			.3306	.0236
[12]	37.3	32.9	.230	−682	1.5952	1.029	(.0241)				.3304	.0234
13	39.9	29.8	.229	−606	1.5911	1.025	.0234				.3298	.0228
14	42.5	26.6	.219	−586	1.5863	1.020	.0222				.3293	.0218
15	45.0	23.7	.213	−542	1.5822	1.015	.0212				.3288	.0209
16	47.4	20.2	.212	−440	1.5787	1.011	.0209	+.65	1.6		.3285	.0207
[17]	49.9	15.6	.201	−351	1.5733	1.005			6.1		.3281	
18	52.4	13.4	.194	−308	1.5699	1.000	.0195		8.5		.3280	.0195
19	55.0	11.0	.184	−264	1.5651	0.9944	.0189				.3276	.0190
20	57.2	9.87	.182	−223	1.5622	.9909			14.4		.3274	
21	59.4	8.29	.173	−195	1.5580	.9865	.0178				.3268	.0180
[22]	61.4	7.61	.166	−193	1.5554	.9827	.0167		18.5		.3268	.0170
23	63.3	6.40	.163	−143	1.5516	.9787	.0166	+1.11	21.4		.3263	.0170
[24]	64.9	5.63	.153	−141	1.5487	.9757	.0162		23.4		.3259	.0166
25	66.7	4.14	.138	−105	1.5407	.9666	.0154	+1.16	30.2		.3249	.0159
26	68.5	3.19	.130	−61	1.5347	.9576	.0144	+1.14	34.9		.3250	.0150
27	70.3	2.78	.121	−61	1.5303	.9542	.0137		36.5		.3239	.0144
[28]	72.3	2.18	.113	−30	1.5264	.9479	.0132		40.7	0.76	.3240	.0139
29	74.1	1.96	.106	−34	1.5236	.9440	.0128	+0.94			.3239	.0136
30	75.9	1.72	.103	−14	1.5215	.9403	.0125		44.2		.3241	.0133

See footnotes at end of table.

TABLE 9.—*Properties of fractions from final extraction process*—Continued

Fraction a	Percent-age extracted b	Kinematic viscosity e at		Kinematic viscosity index	Refractive index d n_D^{25}	Density at 25° C e	Refractive dispersion $n_F - n_C$ at 25° C	Specific optical rotation $[\alpha]_D^{20}$	Aniline point	Solubility in methyl cyanide at 25° C	Specific refraction f $\frac{n^2-1}{n^2+2} \times \frac{1}{d}$	Specific dispersion f $\frac{n_F - n_C}{d}$
		100° F	210° F									
Series C. Charge=666 g. Boiling-point range 1 mm Hg=214° to 218° C—Continued												
		Stokes	*Stokes*			*g/ml*			*°C*	*g/ml of solution*		
31	77.9	1.46	.0971	0	1.5180	.9348	.0123	+.87			.3242	.0132
[32]	80.3	1.22	.0908	14	1.5152	.9287	.0118		48.1		.3248	.0127
33	82.5	1.01	.0806	8	1.5111	.9230	.0117				.3246	.0127
34	84.5	0.863	.0785	35	1.5083	.9177	.0113	+.49			.3250	.0123
35	86.7	.738	.0752	53	1.5056	.9124	.0112		55.9		.3254	.0123
[36]	88.9	.622	.0714	70	1.5023	.9058	.0116	+.30			.3260	.0128
37	91.2	.570	.0674	69	1.4993	.8996	.0106	+.38	62.4		.3266	.0118
38	92.4	----	----		1.4942	.8970	.0099	+1.63	77.5		.3247	.0110
[39+40]	94.8	.907	.0845	51	1.4896	.8958	.0087	+2.97	93.6		.3225	.0097
41	96.3	.631	.0716	68	1.4797	.8774	.0084	+2.14	105.4		.3236	.0096
[Res]	100	.364	.0579	112	1.4711	.8560	.0082	+.81	111.1		.3266	.0096
Series D. Charge=573 g. Boiling-point range at 1 mm Hg=232.4° to 237.4° C.												
Original charge g		14 to 16	0.19 to 0.21	(−155)	(1.563)	(0.989)	(0.0198)	+(0.59)	(29)		(0.328)	(0.0200)
[1]	9.4		0.921		(1.6350)	1.071					.3343	
2	15.8		.660		(1.6270)							
3	18.7		.542		1.6190					2.89		
4	21.2	395	.505	−1,990	1.6143							
5	24.0	289	.481	−1,570	1.6118							
6	27.1	229	.458	−1,350	1.6087							
7	29.6	177	.436	−1.120	1.6053	1.039	.0264				33.16	.0254
8	32.2	136	.410	−952	1.6007							
9	34.6	115	.394	−856	1.5997		.0238	+.50				
10	37.8	82.3	.365	−684	1.5928							
[11]	41.1	67.2	.359	−551	1.5884	1.022	.0227	<−10			.3296	.0222
12	44.2	52.1	.335	−470	1.5842							
13	47.3	40.9	.316	−394	1.5797	1.010	.0201		8.8		.3292	.0199
14	50.4	34.7	.302	−352	1.5752							
15	53.4	27.9	.285	−300	1.5697					1.09		

[16]	56.1	24.0	.279	−251	1.5658	0.9959	.0180	----------	17.4	----------	.3274	.0181
17	58.7	17.7	----------	----------	1.5596							
18	61.0	12.7	.234	−140	1.5553		.0172	+.83	25.9			
19	63.4	9.55	.211	−113	1.5491	.9742	.0163	----------	30.8		.3266	.0167
20	66.1	6.99	.190	−80	1.5427				36.6			
21	68.4	5.44	.174	−58	1.5369							
22	70.6	4.40	.161	−42	1.5315	.9530	.0139	+.65	43.8	.50	.3249	.0146
23	72.9	3.68	.152	−25	1.5277		.0134					
24	75.1	2.98	.141	−8	1.5228		.0125					
[25]	77.6	2.36	.129	7	1.5185	.9344	.0120		54.1		.3246	.0128
26	79.7	1.96	.120	19	1.5144	.9296	.0116		56.8		.3241	.0125
27	81.6	1.66	.113	30	1.5115	.9249	.0113	+.54	59.1		.3242	.0122
[28+29]	85.5	1.29	.101	42	1.5069	.9157	.0112		63.1		.3249	.0122
30	87.9	.994	.0918	60	1.5032	.9083	.0110		65.6	.25	.3256	.0121
31	90.7	.890	.0892	71	1.4998	.9021	.0105	+.50			.3259	.0116
32+33	93.8	1.214	.1028	58	1.4903	.8948	.0093	+2.14	96.7		.3233	.0104
34	95.9	.708	.0814	86	1.4774	.8702	.0084		112.5		.3249	.0097
Res.]	100	.457	.0686	115	1.4707	.8539	.0082	+.40	116.2	.03	.3272	.0096

Series *E*. Charge=514 g. Boiling-point range at 1 mm Hg=251.4° to 258.2° C

Original charge ᵍ	----------	19.4 to 26.3	0.291 to 0.335	(−155)	(1.563)	(0.989)	(0.0197)	----------	(37)	----------	(0.328)	(0.0199)
[1]	8.8					1.074						
2	11.7		1.82		(1.627)							
3	14.4		1.54		(1.622)							
4	17.3		1.55		(1.620)							
5	20.3		1.41		(1.617)							
6	22.5				(1.613)							
7	26.0		1.09		(1.610)							
[8]	29.9		.935		1.6057	1.039	.0255	+0.72		1.52	.3318	.0245
9	32.6	886	.892		1.6025							
10	35.7	576	.813		1.5990							
11	38.7	406	.758		1.5947							
12	41.3	313	.684		1.5900							
[13]	44.3	189	.599	−584	1.5858	1.018			(1.8)	.94	.3296	
14	47.0	149	.570	−486	1.5827							
15	49.2				1.5783							
16	51.8	68.8	.471	−271	1.5719	1.003	.0199		21.1		.3281	.0199
17	54.5	47.4	.425	−202	1.5667							
18	57.3	36.3	.398	−154	1.5617	.9906	.0182		28.1		.3272	.0184
19	59.9	30.6	.371	−142	1.5581							
20	62.4	26.0			1.5547							

See footnotes at end of table.

TABLE 9.—*Properties of fractions from final extraction process*—Continued

Fraction [a]	Percent-age ex-tracted [b]	Kinematic viscosity [c] at 100° F	Kinematic viscosity [c] at 210° F	Kinematic viscosity index	Refractive index [d] n_D^{25}	Density at 25° C [e]	Refractive dispersion $n_F - n_C$ at 25° C	Specific optical rotation $[\alpha]_D^{20}$	Aniline point	Solubility in methyl cyanide at 25° C	Specific refraction [f] $\frac{n^2-1}{n^2+2} \times \frac{1}{d}$	Specific dispersion [f] $\frac{n_F - n_C}{d}$
		Stokes	*Stokes*			*g/ml*			°C	*g/ml of so-lution*		
[21]	65.6	15.5	0.289	−83	1.5491	0.9724	0.0163	----------	37.6	0.45	0.3272	0.0168
22	68.4	12.0	.274	−46	1.5435	.9665	.0157	----------	41.2	----------	.3264	.0162
23	70.6				1.5351							
24	72.6	8.15	----------	----------	1.5299	.9542	.0132	----------	50.0	----------	.3237	.0138
25	75.3	4.51	.187	10	1.5210							
26	77.6	3.56	.171	24	1.5159	.9321	.0117	+.84	63.0	----------	.3240	.0126
[27]	81.6	2.36	.143	41	1.5093	.9203	.0112	----------	68.6	.14	.3246	.0122
28	84.1	2.02	.136	52	1.5065	.9163	.0109	----------			.3245	.0119
29	86.4	1.83	.134	63	1.5050	.9140	.0108	----------	72.7		.3245	.0118
30	88.7	1.43	.122	77	1.5005	.9045	.0106	+.32			.3254	.0117
31+32	92.9	1.54	.125	72	1.4904	.8924	.0090	+1.12	100.1		.3242	.0101
33	95.3	.984	.102	89	1.4776	.8703	.0086	----------	116.9		.3250	.0099
34	97.2	.774	----------	----------	1.4740							
[Res.]	100.0	.659	.0865	111	1.4724	.8560	.0087	+.42	121.6	.02	.3274	.0102

S eries *E*. Charge=514 g. Boiling-point range at 1 mm Hg=251.4° to 258.2° C—Continued

[a] The brackets indicate key fractions on which additional data are given in table 10.

[b] The size of each fraction is given in terms of its location on a scale of 0 to 100 percent for the charge. Fraction *E-2*, for example, constitutes that part of the original charge coming from the extractor at 8.8 to 11.7 percent.

[c] The actual temperatures of these determinations, as measured with a platinum resistance thermometer, were 99.9° and 210.1° F., respectively.

[d] The values of the refractive indices may be converted to other temperatures by using for dn_D/dt the value 0.00038/° C. Over a 5-degree interval this conversion will not introduce an uncertainty greater than ±0.0002, which is, in most cases, about the experimental accuracy.

[e] The values of the density may be converted to other temperatures by using for dD/dt the value 0.0007 g/ml/° C. Over a 5-degree interval this conversion will not introduce an uncertainty greater than ±0.0003 g/ml, which is about the experimental accuracy.

[f] The values for the specific refraction and specific dispersion may be regarded as constant over a 5-degree range of temperature within the accuracy of these measurements.

[g] The properties of the original charge recorded in parentheses were obtained by interpolation from the distillation keys given in table 6.

In table 10 additional data are recorded on 41 key fractions. These data include boiling points, molecular weights, carbon and hydrogen contents, percentages of sulfur plus nitrogen plus oxygen, and the calculated quantities n and x in the formula C_nH_{2n+x}. For some of the fractions, the percentages of sulfur, nitrogen, and oxygen are recorded.

TABLE 10.—*Additional properties of key fractions from final extraction process*

Fraction	Boiling point at 1 mm Hg	Molecular weight	Combustion analyses		Sulfur content [b]	Nitrogen content [b]	Oxygen content [c]	In the formula $C_nH_{2n+x}S_yN_zO_w$				
			Ratio: moles H_2O/CO_2	Mass of sample less mass of C+H				n	x	y	z	w
SERIES A												
	°C			% by wt of sample		% by wt						
Original charge [a]	(185)	(300)	(0.686)	(1.3)	(0.8)	(0.03)	(0.5)	(22.1)	(−13.7)	(0.08)	(0.01)	(0.09)
A–1	185	269	.5397	2.61	1.22	.13	1.26	20.0	−18.42	.10	.02	.21
A–5	186	282	.5792	2.50	1.73	.01	0.76	20.9	−17.56	.15	.00	.13
A–10	---------	298	.6445	1.58	0.92	.01	.65	22.0	−15.65	.09	.00	.12
A–17	---------	318	.7351	0.85	.36	(.01)	.48	23.3	−12.37	.04	.00	.10
A–22	185	329	.7824	.55	.25	.01	.29	24.1	−10.47	.03	.00	.06
A–27	189	348	(.8130)	.67	.28	(.00)	.28	25.4	−9.48	.03	.00	.06
A–res	187	357	.9746	(.69)	---------	---------	---------	25.3	−1.29	---------	---------	---------
SERIES B												
Original charge [a]	(201)	(325)	(0.686)	(1.4)	(0.9)	(0.04)	(0.5)	(23.9)	(−14.9)	(0.09)	(0.01)	(0.10)
B–2	200	281	.5283	2.12	---------	---------	---------	21.0	−19.84	---------	---------	---------
B–6	202	288	.5521	2.49	---------	---------	---------	21.4	−19.18	---------	---------	---------
B–13	202	311	.6183	2.29	---------	---------	---------	22.9	−17.51	---------	---------	---------
B–14	---------	313	.6377	2.13	---------	---------	---------	23.0	−16.68	---------	---------	---------
B–18	---------	326	.6730	1.43	---------	---------	---------	24.0	−15.71	---------	---------	---------
B–21	202	330	.7040	0.91	---------	---------	---------	24.4	−14.42	---------	---------	---------
B–28	---------	354	.7819	.63	---------	---------	---------	25.9	−11.30	---------	---------	---------
B–31	201	360	.8037	.57	---------	---------	---------	26.3	−10.31	---------	---------	---------
B–35	---------	366	.8332	.59	---------	---------	---------	26.6	−8.87	---------	---------	---------
B–res	203	383	.9586	.16	---------	---------	---------	27.4	−2.27	---------	---------	---------

SERIES C

Original charge a	(216)	(347)	(0.691)	(1.4)	(0.9)	(0.06)	(0.4)	(25.5)	(−15.7)	(0.10)	(0.01)	(0.09)
C-1	218	303	.5363	2.63	.77	.56	1.30	22.5	−20.90	.07	.12	.25
C-5	217	312	.5632	2.36	1.49	.08	0.79	23.2	−20.27	.14	.02	.15
C-8		321	.5920	2.42				23.7	−19.35			
C-12	217	329	.6249	2.24	1.50	.02	.72	24.3	−18.21	.15	.00	.15
C-17	216	337	.6708	1.74	(1.1)	(.01)	(.60)	24.8	−16.31	(.10)	.00	(.13)
C-22	217	354	.7128	1.17	0.72	.01	.44	26.0	−14.95	.08	.00	.10
C-24		362	.7269	1.33				26.5	−14.48			
C-28		378	.7793	0.90	.43	(.01)	.47	27.6	−12.19	.05	.00	.11
C-32	215	390	.8073	.60	.31	(.01)	.28	28.5	−10.97	.04	.00	.07
C-36		395	.8392	.70	.37	(.01)	.33	28.7	−9.22	.05	.00	.07
C-39+40	216	412	.9115	.37	.17	.01	.19	29.6	−5.24	.02	.00	.05
C-res	219	420	.9696	.02	(.01)	(.00)	(.01)	30.1	−1.83	.00	.00	.00

SERIES D

Original charge a	(235)	(377)	(0.706)	(1.5)	(0.9)	(0.09)	(0.5)	(27.6)	(−16.2)	(0.11)	(0.02)	(0.12)
D-1		321	.5585	2.66				23.8	−21.04			
D-11	237	361	.6474	2.48				26.4	−18.64			
D-16	235	379	.6919	2.00				27.7	−17.06			
D-25	234	414	.8060	(1.01)				30.1	−11.67			
D-28+29	235	430	.8355	0.64				31.2	−10.26			
D-res	238	457	.9739	.22				32.6	−1.70			

SERIES E

Original charge a	(255)	(415)	(0.712)	(1.6)	(0.9)	(0.13)	(0.6)	(30.5)	(−17.6)	(0.12)	(0.04)	(0.15)
E-1		367	.5666	2.98	.81	.71	1.46	27.1	−23.46	.09	.19	.33
E-8		394	.6249	2.42	(1.3)	.09	(1.03)	29.0	−21.77	(.16)	.03	(.25)
E-13	260	409	.6609	2.15	1.30	.06	0.79	30.0	−20.33	.17	.00	.20
E-21	257	436	.7387	1.44	0.85	.03	.56	31.9	−16.65	.12	.00	.15
E-27	255	469	.8348	0.62	.36	(.01)	.25	34.0	−11.25	.05	.00	.07
E-res	263	496	.9714	.08				35.5	−2.03	.00	.00	.00

a The properties of the original charge given in parentheses were obtained by interpolation from the distillation keys given in table 6.
b The values in parentheses in these columns were estimated.
c The percentage of oxygen was obtained by subtracting the sum of the percentages of carbon, hydrogen, sulfur, and nitrogen from 100.

X. SUMMARY

Although a more complete interpretation of these data in terms of the chemical constitution will follow in a subsequent paper, a few of the more obvious facts may be pointed out here. The extremely wide range in physical properties between the first and last fractions, obtained from the extraction of substantially constant-boiling fractions, is obvious.

The kinematic viscosity at 100° F varies from 248 stokes for fraction C-2 to 0.36 stoke for C-residue, while the viscosity indices for the same fractions vary from $-3,350$ to $+112$. A small maximum occurs for the viscosity index at fractions 36 and 37, and a minimum for the viscosity at fraction 37.

Refractive indices vary from 1.641 to 1.4711 and densities from 1.076 to 0.8560. Dispersions vary from 0.0298 for C-5 to 0.0096 for C-residue.

Optical rotations show interesting maxima and minima. The optical rotation $[\alpha]_D^{20}$, increases from $+0.19$ for C-4 to a maximum of $+1.16$ at C-25, then decreases to a minimum of $+0.30$ for C-36, rises again to a maximum of $+2.97$ for C-39+40, and finally decreases to a minimum of $+0.81$ for the residue. Maxima and minima are also observed for the specific refractions.

Aniline points increase from 1.6° C for C-16 to 111.1° C for C-residue.

Although the boiling points are substantially constant for the fractions from any one series there is a marked increase in molecular weights. For example, for series C, the molecular weights for the first and last fractions are 303 and 420, respectively.

The hydrogen content increases from C-1 to C-residue, the values for the ratio moles H_2O/CO_2 being 0.5363 and 0.9696, respectively. The values for x in the equation C_nH_{2n+x} increase from $x=-20.9$ for C-1 to -1.83 for C-residue. It is interesting to note that sulfur is not concentrated in the first fractions but increases from 0.77 percent for C-1 to a maximum of 1.50 percent in the region from C-5 to C-12 and then decreases to 0.31 for C-32. A slight increase to 0.37 percent for C-36 then occurs. The nitrogenous material, on the other hand, is concentrated in the first few fractions, being 0.56 percent for C-1, 0.08 percent for C-5, and not greater than 0.01 percent for all the fractions beyond about the twelfth.

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